PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference K2292-PCT	**FOR FURTHER ACTION**	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
International application No. PCT/BE 03/00033	International filing date *(day/month/year)* 26.02.2003	Priority date *(day/month/year)* 26.02.2002
International Patent Classification (IPC) or both national classification and IPC C09C3/04		
Applicant K.U. LEUVEN RESEARCH & DEVELOPMENT et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 7 sheets, including this cover sheet.

   ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of 7 sheets.

3. This report contains indications relating to the following items:

   - I ☒ Basis of the opinion
   - II ☐ Priority
   - III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
   - IV ☐ Lack of unity of invention
   - V ☒ Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
   - VI ☐ Certain documents cited
   - VII ☐ Certain defects in the international application
   - VIII ☐ Certain observations on the international application

Date of submission of the demand	Date of completion of this report
11.09.2003	07.05.2004
Name and mailing address of the international preliminary examining authority: European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized Officer Rhodes, K Telephone No. +49 89 2399-8259

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/BE 03/00033

I. Basis of the report

1. With regard to the **elements** of the international application *(Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17))*:

Description, Pages

1-26	as originally filed

Claims, Numbers

1-27	filed with telefax on 11.09.2003
28-63	filed with telefax on 16.01.2004

Drawings, Sheets

1/7-7/7	as originally filed

2. With regard to the **language,** all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

   These elements were available or furnished to this Authority in the following language: , which is:

   ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).

   ☐ the language of publication of the international application (under Rule 48.3(b)).

   ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

   ☐ contained in the international application in written form.

   ☐ filed together with the international application in computer readable form.

   ☐ furnished subsequently to this Authority in written form.

   ☐ furnished subsequently to this Authority in computer readable form.

   ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

   ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

   ☐ the description, pages:

   ☐ the claims, Nos.:

   ☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)).

   (Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-53, 55-63
	No:	Claims	54
Inventive step (IS)	Yes:	Claims	1-53
	No:	Claims	55-63
Industrial applicability (IA)	Yes:	Claims	1-63
	No:	Claims	

2. Citations and explanations

   see separate sheet

Re Item V

Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. **Reference is made to the following documents:**

D1: EP-A-0949217
D2: GB-A-2065157
D3: US-A-3133023

2. **Novelty**

Document D1, which is considered to represent the most relevant state of the art, discloses a method for the reduction in size of granular materials or powders. In said method, the material to be treated is dispersed in a liquid which is circulated through an enclosure wherein which ultrasonic treatment of the suspension occurs (paragraph 10). Table 1 shows the treatment of an aqueous dispersion of fumed silica, from which is seen that a substantial proportion of the agglomerates has been reduced in size by at least 50%. The finer particles thus produced can be incorporated into a mixture for the formation of concrete or mortar (paragraph 26).

The subject-matter of claim 1 differs from the above disclosure in that a magnetic field is employed to reduce the particle size of a suspended compound, as opposed to ultrasonic waves.
The subject-matter of **claims 1-33** is therefore clearly novel (Article 33(2) PCT).

As the method of claims 1-30 is novel, so must an industrial process including the steps of said claims (**claims 34-53**) be novel also.

Document D2 concerns a process for the production of a cement colouring composition. The method comprises forming a mixture of a dispersant and a stabilizer in an aqueous carrier, adding a particulate pigment (for example, iron oxide), and subjecting the mixture to high energy processing to reduce the pigment particles to a micron size range (page 1, lines 32-42). In the resulting thixotropic slurry, the particle size distribution includes largest particles with a

dimension of about 40 µm, large particles with an average size of about 25 µm, smaller particles whose average size is 1-2 µm, and smallest particles down to a minimum size of about 0.5 µm (page 1, lines 74-86). Although it is not stated in D2 in which proportions the various particle sizes are present, it is thought that the high energy milling process will create a substantial amount of smaller particles. Furthermore, it is known in the art that if the particle distribution is higher than the ranges of D2, the colouring strength is adversely affected. It is also known, however, that if the sizes of the particles are below the stated ranges, they may be washed out of dried concrete by normal weather (page 1, lines 86-92).

Claim 54 is a so-called "product-by-process" claim, wherein a product is defined by its method of manufacture, as opposed to by its physical characteristics. Although it is not clear from said claim what these physical characteristics are, they are seen in the description (see, for instance, page 17, lines 3-10). The metallic compound particles or agglomerates are thought to be indistinguishable from those of the prior art (see D2), and can therefore not be novel.

The methods of **claims 55-58**, for evaluating the performance of a magnetic treatment, are not known in the art and are therefore novel.

The apparatus of claim 59 is considered novel over document D3, which concerns the separating of gases from coatings and printing inks containing pigments which respond to magnetic fields (column 1, lines 10-13). This is accomplished by placing a mixture of a ferromagnetic pigment in a magnetic field and manipulating the pigment-vehicle mixture or the magnetic field to cause movement of the powder within the vehicle. One such form of manipulation, namely (a), involves passing the magnetic mixture through the magnetic field. For this to be possible, the apparatus employed must comprise a means for generating a magnetic field and a means for flowing the magnetic mixture through the magnetic field. However, as it is not stated that said means for flowing the mixture is a pump, **claims 59-63** are novel.

3. Inventive Step

The problem to be solved by the present application may be seen as the provision of a method for the production of nanosized particles of metallic compounds.

The method of claim 1 involves the flowing of a fluid, having the metallic compound particles or agglomerates suspended therein, through a magnetic field to solve the posed problem. It is clear from the examples that treatment by the claimed method does indeed result in a reduction in particle size of numerous compounds. As there is no indication in the prior art to solve the problem in this manner, **claims 1-33** are accorded an inventive step (Article 33(3) PCT).

The subject-matter of **claims 34-53** is inventive for the same reasons as outlined for claims 1-30.

Although novel, it is not thought that the processes of claims 59 and 61 are inventive. Measuring the size of particles in suspension before and after a particular treatment is common laboratory and industrial practice, as is measuring the turbidity of a suspension to determine the effectiveness of said treatment. Thus, **claims 55-58** are not thought to be inventive.

Similarly, the apparatus of **claim 59, 62 and 63** is not considered to be inventive over the apparatus of D3. The reasons therefor are as follows: it is considered to be within the ability of the skilled person to employ a pump as the means for passing a magnetic mixture through a magnetic field. The flow rate of the liquid and residence time within the magnetic field provided by the pump are features which are merely chosen from a number of straightforward possibilities from which the skilled person would select, in accordance with circumstances, without the exercise of inventive skill, in order to solve the problem posed.

Furthermore, the features of **claims 60 and 61** are not thought to be inventive, as it is common laboratory and industrial practice to provide an apparatus with means for measuring the size of particles in solution or the turbidity of said solution, when one is interested in evaluating the effectiveness or extent of a given treatment.

4. Industrial Applicability

The current method for reducing the average size of metallic particles or

agglomerates is of clear industrial applicability in a wide range of applications requiring nano- and micro-structured materials.

CLAIMS

1. A method for reducing the average size of metallic compound particles or agglomerates suspended in a fluid by flowing one or more times said fluid having metallic compound particles or agglomerates suspended therein through one or more magnetic fields to reduce the average size of a substantial portion of the metallic compound particles or agglomerates by at least 25 %, preferably at least 50%.

2. A method according to claim 1, wherein the strength of each said magnetic field is at least about 2,000 gauss.

3. A method according to claim 1 or claim 2, wherein said metallic compound is selected from the group consisting of metal oxides, metal hydroxides, metal sulfides, metal selenides, metal tellurides and combinations thereof.

4. A method according to claim 1 or claim 2, wherein said metallic compound is a metal organic or inorganic salt or a metal complex salt.

5. A method according to claim 4, wherein said metal salt or metal complex salt is selected from the group consisting of carbonates, percarbonates, perthiocarbonates, perdicarbonates, perphosphates, perdiphosphates, pergermanates, rhenates, perrhenates, ruthenates, perruthenates, tantalates, pertantalates, technetates, pertechnetates, sulfates, thiosulfates, thiotellurates, sulfites, sulfonates, persulfates, carbides, hydrides, borates, perborates, borohydrides, borosilicates, borotitanates, borotungstates, perchromates, silicates, aluminates, nitrates, nitrites, perazotates, arsenites, arseniates, perarseniates, bromates, bromites, iodates, periodates, iodites, periodohexatungstates, manganates, permanganates, molybdates, permolybdates, perthiomolybdates, vanadates, perthiovanadates, titanates, pertitanates, zirconates, chromates, ferrates, ferricyanates, ferrioxalates, ferrocyanates, ferrofulminates, cobaltocyanates, nickelates, nickelotungstates, platinates, uranates, peruranates, perosmiates, chlorates, perchlorates, chlorites and organic salts of one or more metals of any of groups 1 to 15 of the Periodic Table.

6. A method according to claim 4, wherein said metal salt is a phosphate of one or more metals of any of groups 1 to 11 of the Periodic Table.

7. A method according to any of claims 1 to 6, wherein the average size of said metallic compound agglomerates before performing said method is in a range from about 10 µm to about 100 µm.

8. A method according to any of claims 1 to 7, wherein the average size of a substantial portion of said metallic compound agglomerates after performing said method is reduced to a range from about 0.45 µm to 5 µm.

9. A method according to any of claims 1 to 8, wherein said substantial portion is at least 50% by weight of the suspended agglomerates.

10. A method according to any of claims 1 to 9, wherein the average particle size of said metallic compound particles before performing said method is in a range from about 0.5 µm to about 10 µm.

11. A method according to any of claims 1 to 9, wherein the average particle size of said metallic compound particles after performing said method is reduced to a range from about 0.5 nm to about 500 nm.

12. A method according to any of claims 1, 10 and 11, wherein said substantial portion is at least 20% by weight of the suspended particles.

13. A method according to any of claims 1 to 12, wherein said fluid is a liquid.

14. A method according to any of claims 1 to 13, wherein said fluid is water.

15. A method according to any of claims 1 to 13, wherein said fluid is an organic solvent or a combination thereof with water.

16. A method according to any of claims 1 to 15, wherein said metallic compound particles or agglomerates are suspended in said fluid in the form of a slurry and the concentration of said metallic compound particles or agglomerates in said fluid is at least two times the solubility limit of said metallic compound in said fluid under the physical (temperature, pressure) and chemical (pH) conditions prevailing while flowing said slurry through said magnetic field.

17. A method according to claim 16, wherein said metallic compound is calcium carbonate suspended in the form of an aqueous slurry and its concentration in said slurry if from 50 mg/L to 15 g/L.

18. A method according to claim 16, wherein said metallic compound is calcium hydroxide suspended in the form of an aqueous slurry and its concentration in said slurry is from about 2% to about 15% by weight.

19. A method according to claim 16, wherein said metallic compound is an iron oxide pigment suspended in the form of an aqueous slurry and its concentration in said slurry is from about 0.6% to about 60% by weight.

20. A method according to any of claims 1 to 19, wherein said fluid is a liquid and flowing said liquid through said magnetic field is effected at a temperature between the freezing temperature and the boiling temperature of said fluid under the pressure prevailing while flowing said fluid through said magnetic field.

21. A method according to any of claims 1 to 20, wherein said fluid is water and flowing said liquid through said one or more magnetic fields is effected at a temperature between about 2°C and 95°C under atmospheric pressure.

22. A method according to any of claims 1 to 12, wherein said fluid is a gas.

23. A method according to any of claims 1 to 6, wherein said metallic compound particles are spherical particles.

24. A method according to any of claims 1 to 6, wherein said metallic compound particles are prismatic particles.

25. A method according to any of claims 1 to 24, wherein said fluid includes one or more surfactants.

26. A method according to claim 25, wherein said surfactant is present in an amount such as to produce surfactant-capped nanoparticles.

27. A method according to any of claims 1 to 26, wherein said fluid is re-circulated two or more times through said one or more magnetic fields.

28. A method according to any of claims 1 to 27, wherein the linear flow rate of said fluid through each said magnetic field is between 0.25 and 25 m/s.

29. A method according to any of claims 1 to 28, wherein the residence time of said fluid through each said magnetic field is between 60 microseconds and 10 seconds.

30. A method according to any of claims 1 to 29, wherein the turbidity of the suspension of said metallic compound particles is reduced or the turbidity of the suspension of said metallic compound agglomerates is increased.

31. A method according to any of claims 1 to 6, wherein the metallic compound particles or agglomerates are metallic pigment particles or agglomerates and wherein the average size of a substantial portion of said metallic pigment particles or agglomerates is in a range from 0.5 nm to 5 µm.

32. A method according to claim 31, wherein said metallic pigment is iron oxide.

33. A method according to claim 31 or claim 32, wherein said iron oxide is in its spherical red form or in its prismatic yellow form.

34. An industrial process involving the use of metallic compound particles or agglomerates, comprising a step of reducing by at least 25% the average size of a substantial portion of said metallic compound particles or agglomerates, wherein said step includes a method according to any of claims 1 to 33.

35. An industrial process according to claim 34, wherein said process further comprises one or more post-processing steps performed following the size reducing step.

36. An industrial process according to claim 35, wherein said post-processing step is a heating step.

37. An industrial process according to claim 36, wherein said metallic compound is a metal hydroxide and said heating step raises the temperature of the particles or agglomerates with reduced size sufficiently for converting said metal hydroxide into the corresponding metal oxide.

38. An industrial process according to claim 35, wherein said post-processing step is a drying step for substantially removing the fluid in which the metallic compound particles or agglomerates are suspended during the size reducing step.

39. An industrial process according to claim 35 or claim 38, wherein said post-processing step is a step of mixing an adjuvant together with the optionally dried particles or agglomerates with reduced size.

40. An industrial process according to claim 39, wherein said adjuvant is an electrical conductive powder.

41. An industrial process according to claim 39 or claim 40, wherein mixing is performed by ball milling.

42. An industrial process according to claim 39, wherein said adjuvant is a polymer suitable for ceramer preparation.

43. An industrial process according to claim 39, wherein said adjuvant is a polymerisable alkene matrix monomer suitable for dental and medical restoration.

44. An industrial process according to claim 35 or claim 38, wherein said metallic compound is a semiconductor and said post-processing step is a step of forming a metallic deposit onto the metallic compound particles or agglomerates with reduced size.

45. An industrial process according to claim 35, wherein said post-processing step is a step of diluting the suspension of metallic compound particles or agglomerates with reduced size through the addition of a fluid into said suspension.

46. An industrial process according to claim 35, wherein the fluid used in said diluting step is miscible with the fluid present in the size reduction step.

47. An industrial process according to any of claims 34 to 46, wherein said process further comprises one or more steps of controlling the size of metallic compound particles or agglomerates produced during or after the method according to any of claims 1 to 33.

48. An industrial process according to claim 47, wherein said size controlling step is performed by dynamic light scattering analysis.

49. An industrial process according to claim 47 or claim 48, wherein said process comprises a post-processing step performed following the size reduction step and further comprises one or more steps of controlling the size of metallic compound particles or agglomerates produced during or after said post-processing step.

50. An industrial process according to claim 49, wherein said size controlling step after said post-processing step is performed by dynamic light scattering analysis.

51. An industrial process according to any of claims 47 to 50, wherein said size controlling step is performed in such a way as to measure the average size and/or the size distribution.

52. An industrial process according to claim 35, wherein said post-processing step is a sonication step.

53. An industrial process according to any of claims 34 to 52, wherein said process further comprises one or more steps of controlling the turbidity of the suspension of metallic compound particles or agglomerates involved in said process.

54. Metallic compound particles or agglomerates obtained by a method according to any of claims 1-33 or by an industrial process according to any of claims 34 to 53.

55. A method for evaluating the performance of the method of claim 1, comprising the steps of:

(i) controlling the size of said metallic compound particles or agglomerates suspended in said fluid before said magnetic treatment,

(ii) flowing one or more times said fluid having metallic compound particles or agglomerates suspended therein through said one or more magnetic fields, and

(iii) controlling the size of said metallic compound particles or agglomerates suspended in said fluid after said magnetic treatment.

56. A method according to claim 54, wherein said size controlling step (i) and/or said

size controlling step (iii) is performed in such a way as to measure the average size and/or the size distribution.

57. A method for evaluating the performance of the method of claim 1, comprising the steps of:

(i) controlling the turbidity of said suspension of metallic compound particles or agglomerates before said magnetic treatment,

(ii) flowing one or more times said suspension of metallic compound particles or agglomerates in a fluid through said one or more magnetic fields, and

(iii) controlling the turbidity of said suspension of metallic compound particles or agglomerates after said magnetic treatment.

58. A method according to claim 56, wherein said turbidity controlling step (i) and/or said turbidity controlling step (iii) is performed by determining the proportion of light absorbed by said suspension from a transmitted light beam.

59. An apparatus for performing the method of claim 1, comprising:

- a source of metallic compound particles or agglomerates suspended in a liquid,
- means for generating one or more magnetic fields, and
- a pump for flowing said liquid having metallic compound particles or agglomerates suspended therein one or more times through the one or more magnetic fields.

60. The apparatus of claim 58 further comprising a means for measuring a turbidity of the liquid with metallic compound particles or agglomerates suspended therein.

61. The apparatus of claim 58 or 59, further comprising a means for measuring a particle size of metallic compound particles or agglomerates suspended in the liquid.

62. An apparatus according to any of claims 58 to 60, wherein said pump is for flowing said liquid at a linear flow rate, through each said magnetic field, between 0.25 and 25 m/s.

63. An apparatus according to any of claims 58 to 61, wherein said pump is for flowing said liquid with a residence time of said liquid through each said magnetic field between 60 microseconds and 10 seconds.